

Statistical and Low Temperature Physics (PHYS393)

4. Indistinguishable particles and the ideal gas.

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4.1 Indistinguishable particles

4.2 Counting states

4.3 Ideal gas

4.4 Partition function

4.5 Boltzmann constant

4.6 Diatomic ideal gas

4.7 Exercises

Aim

To understand the effect of indistinguishable particles on the statistics, and to apply this to the ideal gas.

Objectives

1. To explain the counting of states and derive the density of states.
2. To explain the conditions under which the ideal gas model would not be valid.
3. To derive the Maxwell-Boltzmann distribution.
4. To derive the heat capacity for mono and diatomic gases.
5. To explain the effects of ortho and parahydrogen.

4.1 Indistinguishable particles

Indistinguishable particles are identical particles.

It is not possible to tell one from the other.

There is a special case. If they fixed in a solid, as with the paramagnet that we have seen previously, then we can tell them apart with the help of their location. In that case, however, they become distinguishable particles.

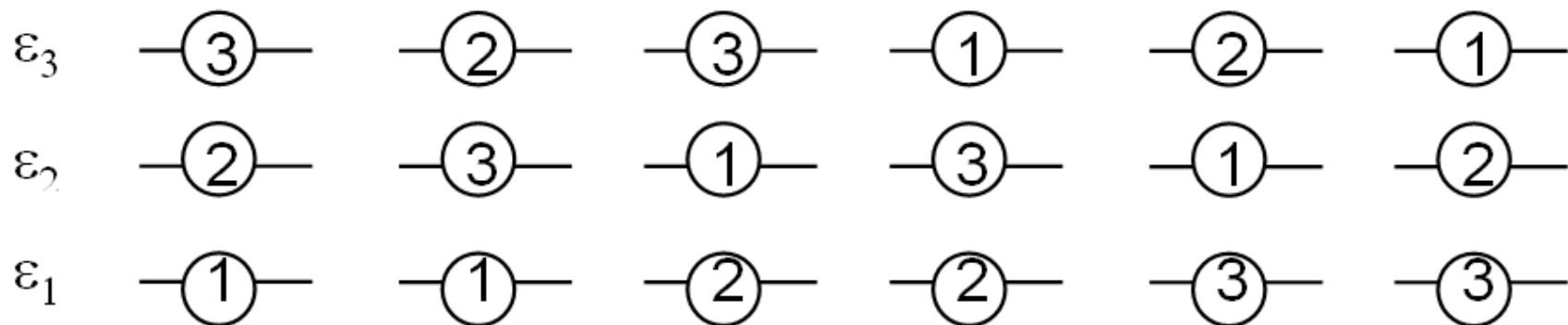
We are therefore interested in cases when they are not fixed. Examples are atoms in a gas, electrons in a metal, and photons in a cavity.

We shall start with the monatomic ideal gas. Each particle in this gas is a single atom.

How are they different from distinguishable particles?

Suppose that there are 3 particles, each with 3 energy levels ϵ_1 , ϵ_2 and ϵ_3 .

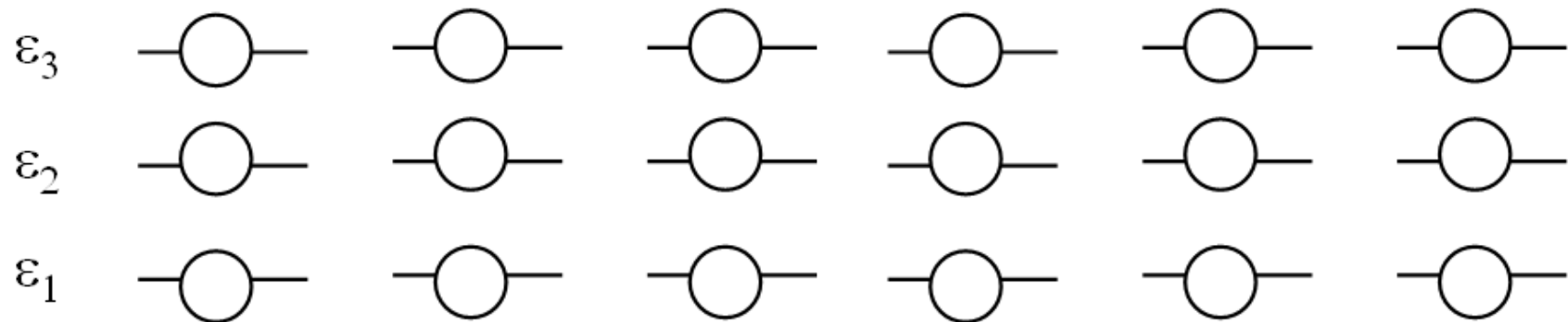
Consider the macrostate $n_1 = 1$, $n_2 = 1$ and $n_3 = 1$. I.e. each level has one atom:



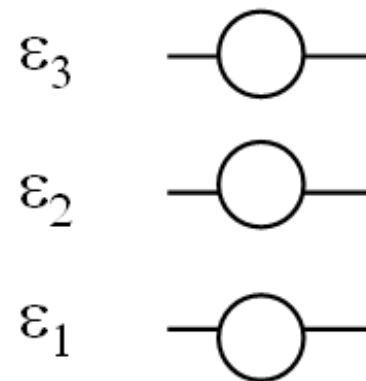
If the particles are distinguishable, then there are 6 microstates.

However, if the particles are indistinguishable, there is only 1.

Just erase the numbers - they all look the same!



So there is really just one microstate:



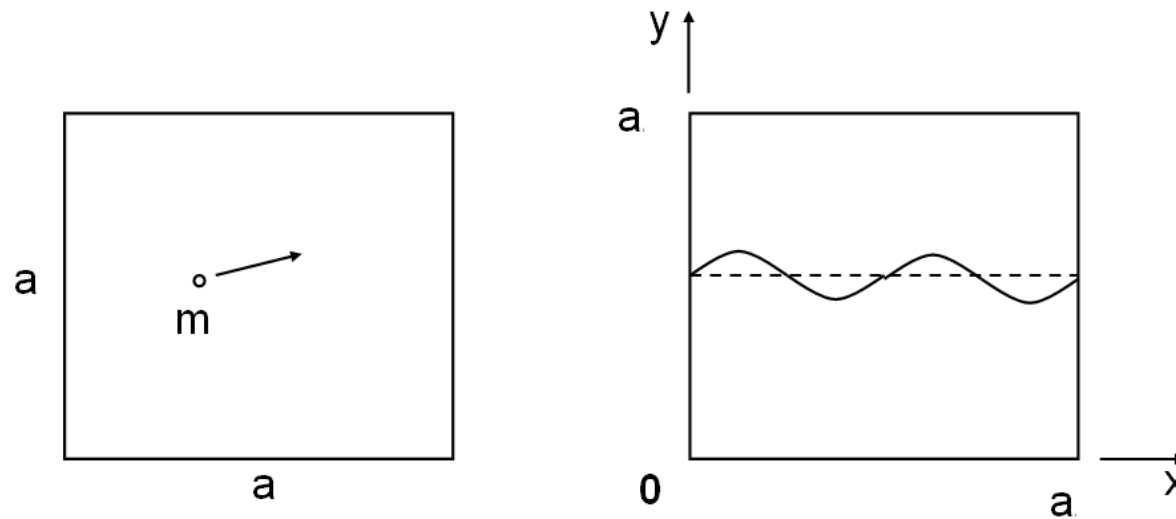
There are a few steps to deriving the statistics for an ideal gas:

1. We start with a single atom in a 3-D box. We solve Schrödinger's equation and obtain the energy states.
2. At room temperature, these energy states would be very close together. They get even closer at higher energy. We need to find the density of states, which gives the number states per unit energy.
3. It turns out that the large density of energy states means that it is very unlikely for any two atoms to even occupy the same levels. This makes it possible to simplify the calculation and obtain the energy distribution of the atoms.

4.2 Counting states

A particle in a 3-D box

We first determine the energy states for a particle in a 3-D box.



We solve Schrödinger's equation for the particle:

$$-\frac{\hbar^2}{2m} \left(\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} \right) + V\psi = E\psi$$

where V is zero in the box, and infinite at the walls. So the wave function must have zero amplitude there.

Energy states of the particle

This is done in the standard way by trying the solution

$$\psi = \sin k_x x \sin k_y y \sin k_z z$$

where (k_x, k_y, k_z) are unknown constants. They can be determined from the boundary condition that the wave function must have zero amplitude at the wall.

In the x direction, suppose the walls are at $x = 0$ and $x = a$. The condition can be written as:

$$\sin k_x a = 0.$$

This gives

$$k_x a = n_x \pi \quad \text{or} \quad k_x = \frac{n_x \pi}{a},$$

where n_x is a positive integer. This means that k_x is quantised. Similarly, for the y and the z directions, we find

$$k_y = \frac{n_y \pi}{a} \quad \text{and} \quad k_z = \frac{n_z \pi}{a}.$$

We can then substitute the solution

$$\psi = \sin k_x x \sin k_y y \sin k_z z$$

into the Schrödinger's equation

$$-\frac{\hbar^2}{2m} \left(\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} \right) + V\psi = E\psi$$

to find the energy. This gives

$$\frac{\hbar^2}{2m} (k_x^2 + k_y^2 + k_z^2) = E.$$

It can also be written in the form

$$\frac{\hbar^2 k^2}{2m} = E$$

where

$$k^2 = k_x^2 + k_y^2 + k_z^2.$$

k is called the wavevector.

We have obtained the energy of the particle:

$$E = \frac{\hbar^2}{2m}(k_x^2 + k_y^2 + k_z^2)$$

and the components of the wavevector:

$$k_x = \frac{n_x\pi}{a}, \quad k_y = \frac{n_y\pi}{a} \quad \text{and} \quad k_z = \frac{n_z\pi}{a}.$$

Substituting, we get

$$\varepsilon_{n_x n_y n_z} = \frac{h^2}{8ma^2}(n_x^2 + n_y^2 + n_z^2).$$

E is replaced by the symbol $\varepsilon_{n_x n_y n_z}$. This is to indicate that it is quantised, and depends on the positive integers (n_x, n_y, n_z) .

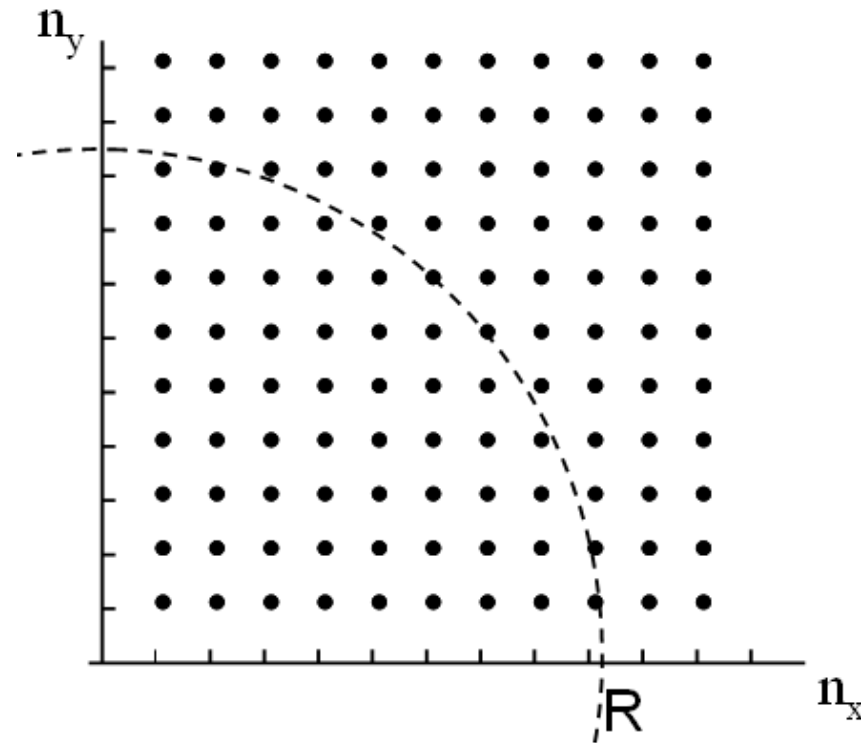
We need a way to determine the number of states below a certain energy, ε . This would then allow us to find the density of states.

To develop the idea, start from the simpler case in 2-D. If we consider a particle in a 2-D box, the energy would be

$$\varepsilon_{n_x n_y} = \frac{h^2}{8ma^2}(n_x^2 + n_y^2)$$

Notice that n_z has been left out. We can represent the possible energy states by treating (n_x, n_y) as co-ordinates, and plotting them on a graph:

Counting states in 2-D

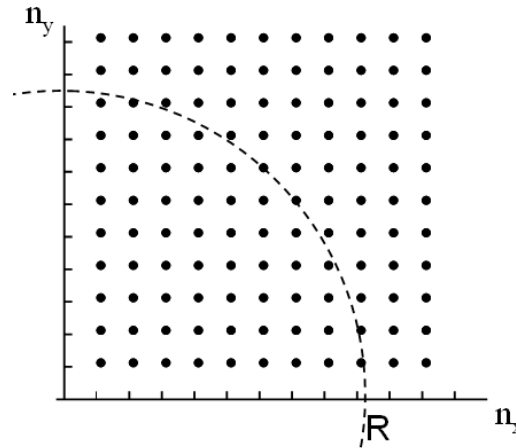


Remember that (n_x, n_y) must be positive integers. So the points are 1 unit distance apart.

If we draw a circle of radius R , it would be described by the equation

$$R^2 = n_x^2 + n_y^2.$$

Counting states in 2-D



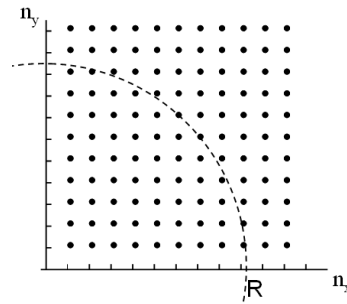
Compare the equations for the circle and for the energy:

$$R^2 = n_x^2 + n_y^2$$
$$\frac{8ma^2\varepsilon_{n_x n_y}}{h^2} = n_x^2 + n_y^2$$

If we associate the energy with the radius: $R^2 = 8ma^2\varepsilon/h^2$

we could find the number of states below that ε , by counting the number of points enclosed by the circle.

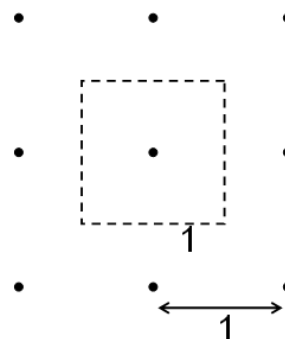
Counting states in 2-D



Note that all the points are in the first quadrant only.

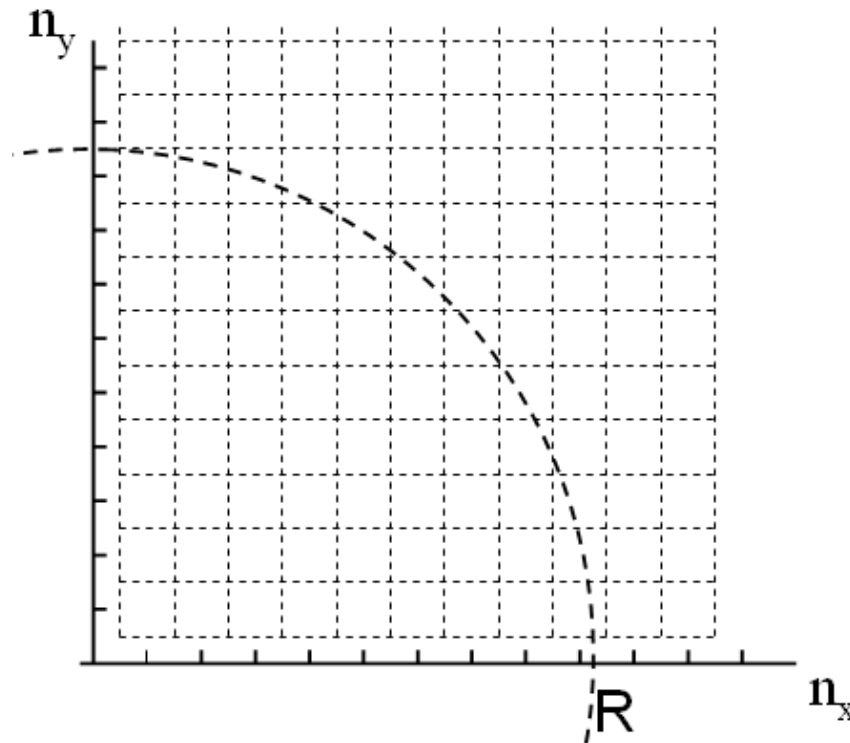
Note also we shall assume R is much larger than the distance between adjacent points. (We would need to justify this later.)

The distance between adjacent points is 1 unit. Consider a unit square centred at the point.



Counting states in 2-D

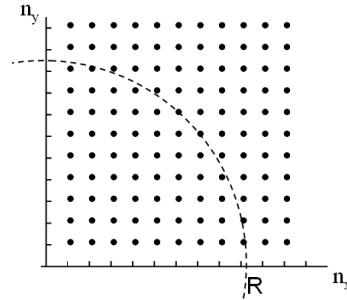
If we draw such a square for every point, the squares would fill up the whole quadrant.



Instead of counting the points, we can count the squares.

Since the area of each square is 1, the number of squares would just be the area of the first quadrant, $\pi R^2/4$.

Counting states in 2-D



Since the number of states is the number of points, this number is also $\pi R^2/4$.

Recall the relation between energy and radius: $R^2 = 8ma^2\varepsilon/h^2$.

Therefore, in 2-D, the number of states below ε is:

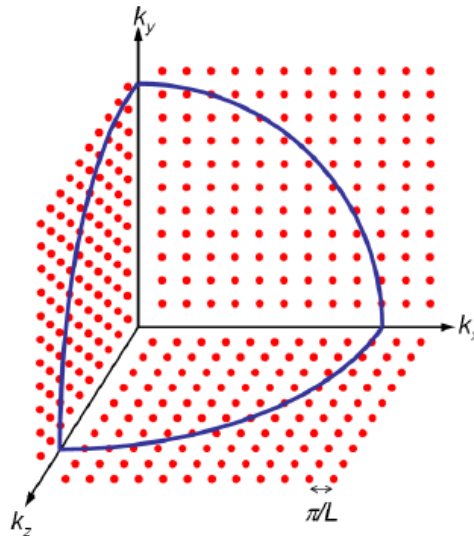
$$G(\varepsilon) = 2\pi ma^2\varepsilon/h^2.$$

Counting states in 3-D

In 3-D, the energy states are given by:

$$\frac{8ma^2\varepsilon_{n_x n_y}}{h^2} = n_x^2 + n_y^2 + n_z^2$$
$$R^2 = n_x^2 + n_y^2 + n_z^2$$

Compare this with the equation of a sphere.



Since (n_x, n_y, n_z) are positive, the states are given by the points in the first octant (1/8) of the sphere.

Next, we need to work out how to count the states in 3-D. We need to make the following changes:

1. (n_x, n_y) to (n_x, n_y, n_z)
2. Points in 2-D to points in 3-D
3. Circle to sphere.
4. Quadrant to octant (1/8 of a sphere).
5. Unit square to unit cube.
6. Area to volume.

The formulae are as follows:

1. $1/8$ of the volume of a sphere is $\frac{1}{8} \times \frac{4}{3}\pi R^3$.

2. The relation between energy and radius remains the same:

$$R^2 = \frac{8ma^2\varepsilon}{h^2}$$

3. In 3-D, a unit cube is associated with each state. So the number of states is the volume of the octant:

$$\begin{aligned} G(\varepsilon) &= \frac{1}{8} \times \frac{4}{3}\pi \left(\frac{8ma^2\varepsilon}{h^2} \right)^{3/2} \\ &= \frac{4\pi V}{3h^3} (2m\varepsilon)^{3/2} \end{aligned}$$

where $V = a^3$.

We can now find the density of states. We have found that the total number below energy ε is

$$G(\varepsilon) = \frac{4\pi V}{3h^3} (2m\varepsilon)^{3/2}$$

If we increased the energy by $\delta\varepsilon$, this number would change by $\delta G(\varepsilon)$.

The density of state is the number of states per unit energy. Therefore this is given by $\delta G(\varepsilon)/\delta\varepsilon$, or

$$g(\varepsilon) = dG(\varepsilon)/d\varepsilon = \frac{4m\pi V}{h^3} (2m\varepsilon)^{1/2}$$

4.3 Ideal gas

We should now justify our assumption that it is very unlikely for two atoms to occupy the same energy state.

At a temperature T , we know from simple kinetic theory of ideal gas that the average energy of a gas atom is about $3k_B T/2$.

First, we need to know how many energy states there are below this energy at room temperature. We can use the formula we have derived:

$$G(\varepsilon) = \frac{4\pi V}{3h^3} (2m\varepsilon)^{3/2}$$

by setting $\varepsilon = 3k_B T/2$.

$$G(3k_B T/2) = \frac{4\pi V}{3h^3} (2m\varepsilon)^{3/2}$$

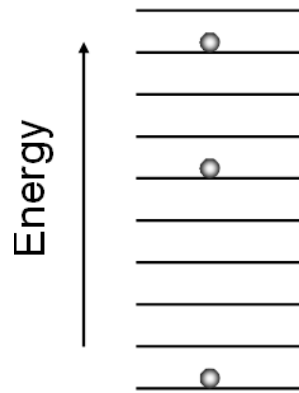
Putting in the numbers for one mole of ideal gas at room temperature, we find that the number of states below $3k_B T/2$ is about 10^{30} .

1 mole of gas contains about 10^{24} atoms.

This means we have about $10^{30} \div 10^{24} = 10^6$ states per atom.

Ideal gas energy states

This means we have about 1 million energy states for every atom.

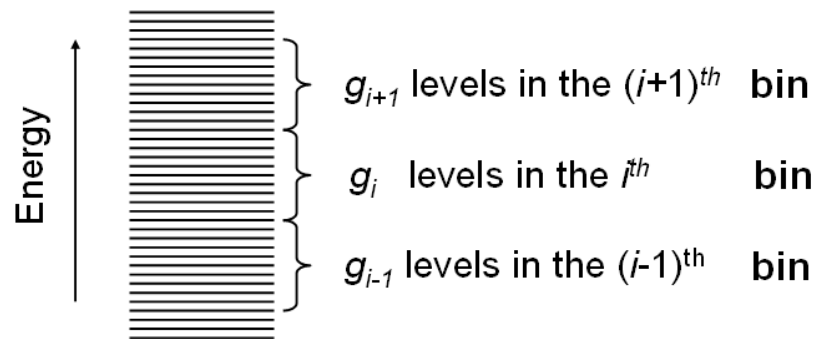


So it is extremely unlikely that two atoms would ever occupy the same energy state.

We are now going to derive the energy distribution of these atoms.

Grouping energy levels into bundles

We shall borrow the idea from histograms - divide the energy levels into bins, or bundles.

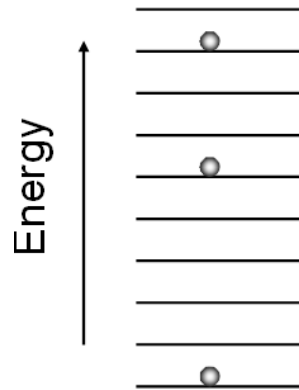


Suppose each bundle covers an energy interval $d\varepsilon$.

We want to find out how many ways we can arrange a number of atoms in a particular bundle.

Energy levels as partitions

Consider the i^{th} bundle. There are g_i energy states and n_i atoms.



Recall that it is extremely unlikely for two atoms to be in the same state.

Think of each state as a partition. The partition and the atom are like two different objects. We need to find the number of ways to arrange n_i atoms and g_i partitions in a row.

Number of arrangements

There are n_i atoms and g_i partitions.

We can use the combination formula ${}^nC_r = \frac{n!}{r!(n-r)!}$.

This gives, for one bundle, $\frac{(n_i+g_i)!}{n_i!g_i!}$ ways.

To find the total number of arrangements for all bundles, we must multiply together the answer for every bundle:

$$\Omega = \prod_i \frac{(n_i + g_i)!}{n_i!g_i!} \quad (1)$$

Since the number of energy states in each bundle is much larger than the number of atoms, $g_i \gg n_i$, we can simplify this.

Expand

$$\Omega = \prod_i \frac{(g_i + n_i) \dots (g_i + 1)(g_i) \dots (1)}{n_i! g_i!} = \prod_i \frac{(g_i + n_i) \dots (g_i + 1)}{n_i!}$$

Since $g_i \gg n_i$, $(g_i + n_i) \approx g_i$ and $(g_i + 1) \approx g_i$. Therefore

$$\Omega = \prod_i \frac{g_i^{n_i}}{n_i!}$$

This gives the number of microstates in the macrostate n_i .

$$\Omega = \prod_i \frac{g_i^{n_i}}{n_i!}$$

If a macrostate is specified by (n_1, n_2, n_3, \dots) , or n_i in short, then the above expression gives the number of microstates in the macrostate.

We are interested in the most likely distribution of (n_1, n_2, n_3, \dots) , or the most probable macrostate.

We can once again apply the Lagrange multiplier to find this.

Most probable macrostate for the ideal gas

We apply the Lagrange multiplier method as follows:

1. Instead of Ω , maximise $\ln \Omega$.
2. Apply Stirling's approximation:

$$\ln \Omega = \sum_i [n_i \ln g_i - n_i \ln n_i + n_i] = \sum_i n_i \ln(g_i/n_i) + N$$

3. The number of particles is fixed:

$$N = \sum_i n_i$$

4. The total energy is fixed:

$$U = \sum_i n_i \varepsilon_i.$$

5. Define the Lagrange function as $\ln \Omega + \lambda_1 N + \lambda_2 U$.
6. To find the maximum, differentiate with respect to n_i :

$$\ln g_i - \ln n_i + \lambda_1 + \lambda_2 \varepsilon_i = 0$$

We have found

$$\ln g_i - \ln n_i + \lambda_1 + \lambda_2 \varepsilon_i = 0$$

Rearranging, we get

$$n_i = A g_i \exp(\lambda_2 \varepsilon_i),$$

where

$$A = \exp(\lambda_1).$$

In the same way as before, by using our knowledge of entropy, we can show that

$$\lambda_2 = -\frac{1}{k_B T}.$$

This gives the Boltzmann distribution again:

$$n_i = A g_i \exp(-\varepsilon_i / k_B T),$$

Approximate to continuous energy

We are mainly interested in the energy range of the order of $k_B T$ (which means up to a few times of that). Most of the atoms would fall in this range.

We have seen previously that there is a very large number of energy states in this range.

Since the energy levels are so closely spaced, we can approximate them to continuous energy.

We have previously obtained the density of states, which is the number of states per unit energy, $g(\varepsilon)$.

Consider the i^{th} bundle. Assume that this occupies an energy interval of $d\varepsilon$.

The number of energy states is then given by $g_i = g(\varepsilon)d\varepsilon$.

In a similar way, we can define a number density $n(\varepsilon)$ as the number of particles per unit energy.

So the number of atoms in the bundle would be

$$n_i = n(\varepsilon)d\varepsilon.$$

Therefore, the distribution that we have obtained,

$$n_i = Ag_i \exp(-\beta\varepsilon_i),$$

can be rewritten as

$$n(\varepsilon)d\varepsilon = Ag(\varepsilon) \exp(-\varepsilon_i/k_B T)d\varepsilon$$

Substituting the formula for $g(\varepsilon)$, we get

$$n(\varepsilon) = A \frac{4m\pi V}{h^3} (2m\varepsilon)^{1/2} \exp(-\varepsilon/k_B T)$$

Note that the total number of atoms is then given by integrating over all energy:

$$N = \int_0^\infty n(\varepsilon) d\varepsilon$$

This relation is known as the normalisation condition.

The unknown constant A can be determined by integrating the normalisation condition (with the help of the table of integrals):

$$A = \frac{N}{V} \left(\frac{h^2}{2\pi m k_B T} \right)^{3/2}$$

This gives

$$n(\epsilon) = \frac{2\pi N}{(\pi k_B T)^{3/2}} (\epsilon)^{1/2} \exp(-\epsilon/k_B T)$$

The energy is just the kinetic energy, $\epsilon = mv^2/2$. So

$$n(v) = N \left(\frac{2}{\pi} \right)^{1/2} \left(\frac{m}{k_B T} \right)^{3/2} \exp(-mv^2/2k_B T) v^2$$

This is the Maxwell-Boltzmann distribution of speeds.

There is actually a simpler way to derive the Maxwell-Boltzmann distribution, without using Lagrange multipliers.

You can find it here:

http://galileo.phys.virginia.edu/classes/252/kinetic_theory.html

At the Columbia University in New York,

Miller and Kusch measured the speeds of the atoms in potassium vapour. They agree very well with the formula.

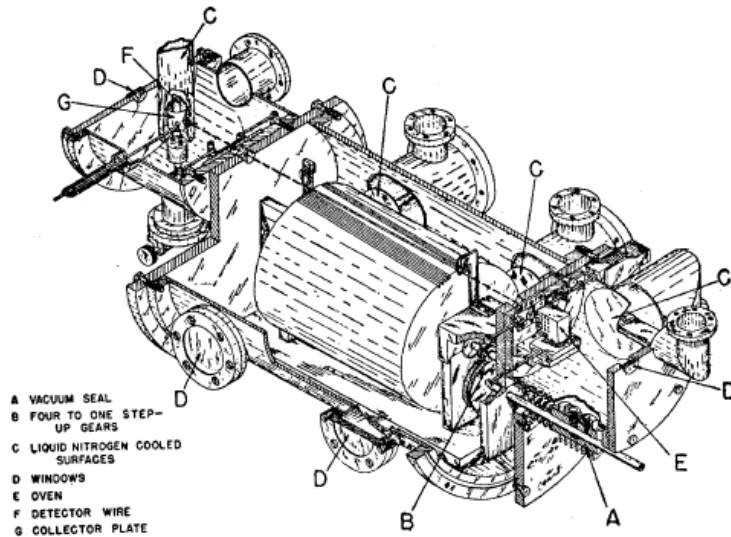


FIG. 2. Schematic diagram of the apparatus designed to measure velocity distributions.

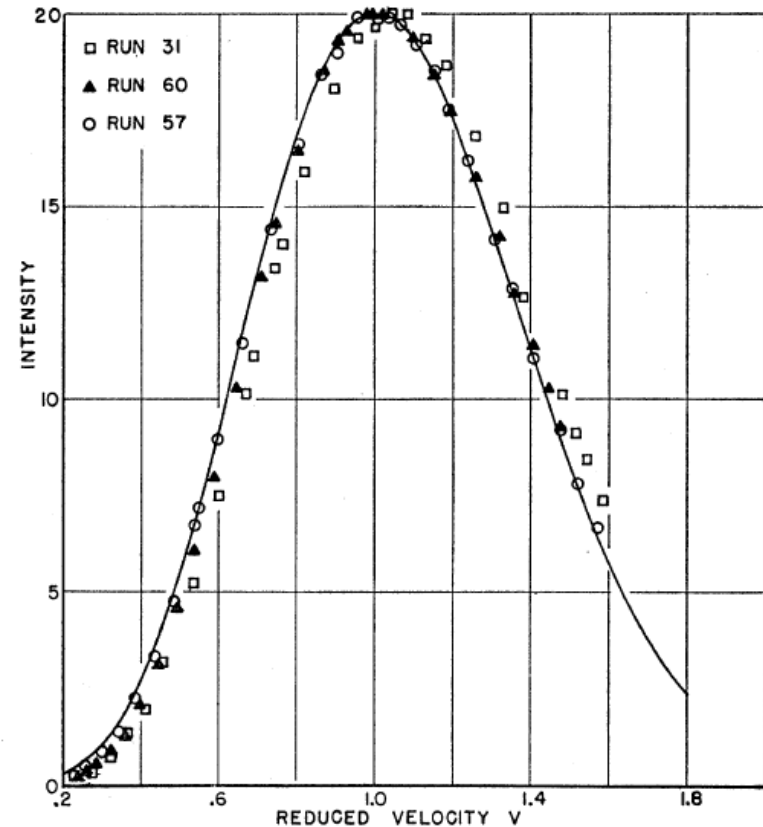
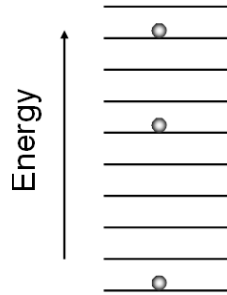


FIG. 4. Typical potassium velocity distributions. The vapor pressures in the ovens are given in Table II. Run 31 was made with thick oven slits and runs 57 and 60 with thin slits.

This was published in Physical Review in 1955.

When would it break down?

We have assumed that: "It is extremely unlikely that two atoms would ever occupy the same energy state."



Recall that we have arrived at this by looking at the number of states below the mean energy $3k_B T/2$, when T is at room temperature.

If T is very small, there may be far fewer states below the mean energy. Then it would be very likely for two atoms to occupy the same state, and the Maxwell-Boltzmann distribution would not be valid.

Instead, quantum statistics - such as Fermi-Dirac or Bose-Einstein - have to be used. We shall learn about these later.

A note on the recommended text

If you are using the recommended text:

Statistical Mechanics - A Survival Guide,
by A. M. Glazer and J. S. Wark

please note that the Lagrange multiplier method given on page 49 is incorrect.

Please use the version given in these lectures.

4.4 Partition function

The partition function would be useful for deriving the macroscopic quantities like heat capacity, pressure and entropy from the microscopic properties.

It would also be useful for extending the calculation to diatomic gases, and include effects like rotation, vibration and even nuclear spin states.

In the lectures on paramagnetic salts, we have derived formulae for energy and entropy in terms of the partition function. The same formulae, unfortunately, cannot be used for the ideal gas. The reason is related to the fact that the particles in the ideal gas are indistinguishable.

The partition function

To see how to obtain the partition function for the ideal gas, we first rewrite the formulae for the paramagnetic salts:

Total energy

$$U = Nk_B T^2 \frac{\partial \ln Z}{\partial T}$$

Entropy

$$S = Nk_B \ln Z + Nk_B T \frac{\partial \ln Z}{\partial T}$$

Helmholtz free energy

$$F = -Nk_B T \ln Z$$

Notice all of these formulae contain the term $N \ln Z$. Rewrite this as

$$N \ln Z = \ln Z^N.$$

Z^N is called the system partition function. Denote this by Z_N .

The partition function

In terms of the system partition function, the formulae can be written as follows:

Total energy

$$U = k_B T^2 \frac{\partial \ln Z_N}{\partial T}$$

Entropy

$$S = k_B \ln Z_N + k_B T \frac{\partial \ln Z_N}{\partial T}$$

Helmholtz free energy

$$F = -k_B T \ln Z_N$$

In the case of the ideal gas, the system partition function has to be replaced by

$$Z_N = \frac{Z^N}{N!}.$$

The reason is related to the fact that the particles are indistinguishable. Dividing by $N!$ would avoid overcounting.

The partition function

In terms of the system partition function, we can continue use the same formulae for energy, entropy. and free energy.

The difference is that, for distinguishable particles, the system partition function is

$$Z_N = Z^N,$$

whereas for indistinguishable particles, the system partition function is

$$Z_N = \frac{Z^N}{N!}.$$

For convenience, we may refer to the original partition function Z as the single particle partition function.

We have previously written the single particle partition function as a summation:

$$Z = \sum_i \exp\left(-\frac{\varepsilon_i}{k_B T}\right).$$

For the ideal gas, the spacing between energy levels are small compared to $k_B T$. So the summation may be approximated by an integration:

$$Z = \int_0^\infty g(\varepsilon) \exp\left(-\frac{\varepsilon}{k_B T}\right) d\varepsilon$$

The heat capacity

Substituting the density of states,

$$Z = \int_0^\infty \frac{4m\pi V}{h^3} (2m\varepsilon)^{1/2} \exp\left(-\frac{\varepsilon}{k_B T}\right) d\varepsilon$$

This can be integrated with the help of the table of integrals:

$$Z = V \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2}$$

Recall that there is a set of formulae that we can use to find the energy and entropy from the partition function. The energy is then given by this formula:

$$U = k_B T^2 \frac{\partial \ln Z_N}{\partial T}$$

Substituting the system partition function $Z^N/N!$, we find

$$U = \frac{3Nk_B T}{2}.$$

The heat capacity is then obtained by differentiating with respect to temperature:

$$C = \frac{dU}{dT} = \frac{3}{2}Nk_B.$$

This agrees with the result from kinetic theory of the ideal gas.

http://en.wikipedia.org/wiki/Kinetic_theory.

Next, we shall show that we can derive the ideal gas law

$$pV = nRT$$

using the partition function. In order to do so, we shall use the Helmholtz free energy to calculate the pressure p .

Recall from the lectures on paramagnetic salts that the differential of the Helmholtz free energy is:

$$dF = -SdT - pdV.$$

which leads to this formula for p :

$$\left(\frac{\partial F}{\partial V}\right)_T = -p.$$

Here is a list of all the formulae we would need:

To find the pressure from the Helmholtz free energy:

$$\left(\frac{\partial F}{\partial V}\right)_T = -p.$$

The partition function for the Helmholtz free energy:

$$F = -k_B T \ln Z_N,$$

The system partition function for indistinguishable particles:

$$Z_N = \frac{Z^N}{N!}.$$

The partition function for the ideal gas:

$$Z = V \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2}$$

Substituting the system partition function

$$Z_N = \frac{Z^N}{N!}$$

into the Helmholtz free energy formula

$$F = -k_B T \ln Z_N,$$

we find

$$F = -k_B T (N \ln Z - \ln N!).$$

To see what $\ln Z$ looks like, we substitute the partition function

$$Z = V \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2}.$$

This gives:

$$\ln Z = \ln V + \text{terms not containing } V.$$

In order to find the pressure p , we need to take the partial derivative with respect to V :

$$\left(\frac{\partial F}{\partial V}\right)_T = -p.$$

So terms that do not contain V would vanish. Substituting the expression for $\ln Z$ into the equation for the Helmholtz free energy formula, we find

$$F = -Nk_B T \ln V + \text{terms not containing } V.$$

Differentiating with respect to V , we get

$$\left(\frac{\partial F}{\partial V}\right)_T = -\frac{Nk_B T}{V}.$$

Since this partial derivative is equal to $-p$, we have

$$-p = -\frac{Nk_B T}{V}.$$

Rearranging, we have the ideal gas law:

$$pV = Nk_B T$$

To write this in the more conventional form, we know that the Boltzmann constant is

$$k_B = \frac{R}{N_A},$$

where R is the gas constant and N_A is the Avogadro constant. We also know that the number of moles N is related to the number of particles n by

$$N = nN_A.$$

Substituting these, into the above equation for p , we get the more conventional form of the ideal gas law:

$$pV = nRT.$$

4.5 Boltzmann constant

We can now return to the earlier lectures on derivation of the Boltzmann distribution

$$n_i = A \exp(-\varepsilon_i/k_B T)$$

and tie up a loose end.

Recall that the $k_B T$ in the Boltzmann factor comes from one of the Lagrange multipliers:

$$\lambda_2 = \frac{1}{k_B T}.$$

We have seen how this is related to temperature T using our knowledge on entropy.

Boltzmann constant

We have also seen that there should be a constant,

$$\lambda_2 = \frac{1}{k_B T}.$$

but we have not looked at why the constant should be the Boltzmann constant

$$k_B = \frac{R}{N_A}$$

where R is the gas constant and N_A is the Avogadro's constant. We are ready to do that now.

Recall that we have derived the following form of the ideal gas law:

$$pV = Nk_B T.$$

We have derived this from the formula for the Helmholtz free energy expressed in terms of the partition function. So the Boltzmann constant k_B here originates from the Lagrange multiplier.

The ideal gas law, on the other hand, may be viewed as an empirical law:

$$pV = nRT.$$

Under suitable conditions, the gas constant R can be measured using real gases, and has the value of $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$.

Think of k_B as an unknown constant from the Lagrange multiplier. We can find it by comparing the empirical law above, with the gas law that is derived using the partition function:

$$pV = Nk_B T.$$

Comparing the above 2 equations, we find

$$Nk_B = nR.$$

Boltzmann constant

Since the number of moles n is related to the number of particles N by

$$n = \frac{N}{N_A},$$

we have

$$Nk_B = \frac{N}{N_A}R$$

and finally, we obtain the value for k_B :

$$k_B = \frac{R}{N_A},$$

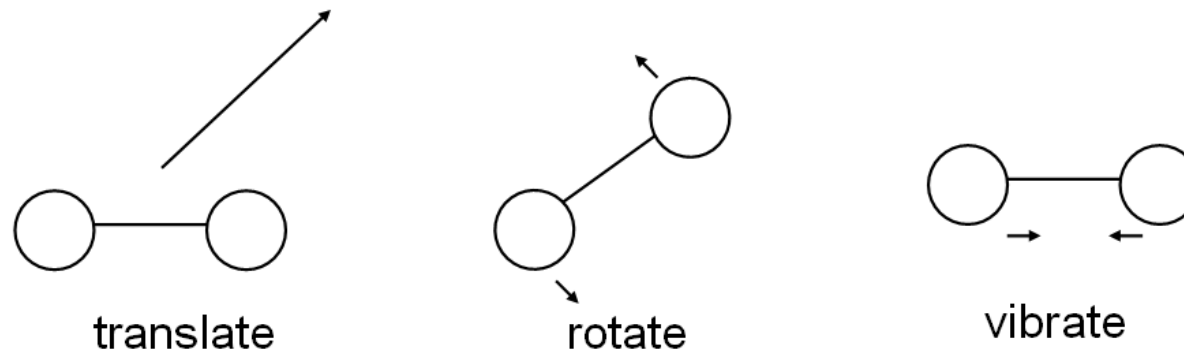
which is indeed the Boltzmann constant as we have assumed.

We should note that the ability to derive the ideal gas law from the partition function is one of the successes of statistical mechanics. It is evidence that our rather abstract ideas about probabilities, microstates and Lagrange multipliers do give a realistic description of the actual behaviour of real gases.

4.6 Diatomic ideal gas

Diatomic ideal gas

The molecule of a diatomic gas has two atoms bonded together. Additional types of movements, or degrees of freedom, are possible.



For the monatomic gas, the atom has only translation motion. In the diatomic gas, the molecule also has rotation and vibration.

The total energy is: $\epsilon_{\text{total}} = \epsilon_{\text{trans}} + \epsilon_{\text{rot}} + \epsilon_{\text{vib}}$

More details about diatomic molecules can be found here:

http://en.wikipedia.org/wiki/Diatomic_molecule

Partition function for diatomic gas

The probability of being in a particular total energy level can be found by multiplying the probabilities in the separate levels:

$$\begin{aligned} g_{\text{total}} \exp(-\varepsilon_{\text{total}}/k_B T) &= \\ g_{\text{trans}} \exp(-\varepsilon_{\text{trans}}/k_B T) &\times g_{\text{rot}} \exp(-\varepsilon_{\text{rot}}/k_B T) \times g_{\text{vib}} \exp(-\varepsilon_{\text{vib}}/k_B T) \end{aligned}$$

g_{trans} is the same density of states that we have seen previously for the monatomic gas.

g_{rot} and g_{vib} are the density of states for rotation and vibration respectively.

This means that the partition function can be written as

$$Z = Z_{\text{trans}} \times Z_{\text{rot}} \times Z_{\text{vib}} = Z = V \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} \times Z_{\text{rot}} \times Z_{\text{vib}}$$

Rotational energy levels

We know from quantum mechanics that the rotational energy levels are

$$\varepsilon_J = \frac{\hbar^2}{2I} J(J + 1)$$

where J is an integer and I the moment of inertia of the molecule.

We also know that the components in the z direction are quantised, with quantum numbers: $m_J = -J, J - 1, \dots, +J$.

So there are $(2J + 1)$ states associated with the same energy level J . We say that there is a degeneracy of $(2J + 1)$.

For example, for the angular momentum $J = 1$, there would be $(2J + 1) = 3$ states with this angular momentum. These correspond to the components $m_J = -1, 0, 1$. So we say that the angular momentum $J = 1$ has a degeneracy of 3.

The rotational partition function is then given by

$$Z_{\text{rot}} = \sum_{J=0}^{\infty} (2J + 1) \exp[-\hbar^2 J(J + 1)/2Ik_B T]$$

We can understand this by looking at the term $J = 1$ again. The Boltzmann factor for $J = 1$ would be

$$\exp[-\hbar^2 J(J + 1)/2Ik_B T] = \exp(-\hbar^2/Ik_B T).$$

Since there are $(2J + 1) = 3$ states for the same $J = 1$, there are 3 states with the same Boltzmann factor. So the $J = 1$ would contribute 3 times of the Boltzmann factor $\exp(-\hbar^2/Ik_B T)$ to the partition function.

In general, for the angular momentum J , there would be $(2J + 1)$ with the same Boltzmann factor. So this would contribute $(2J + 1)$ times of the Boltzmann factor $\exp[-\hbar^2 J(J + 1)/2Ik_B T]$ to the partition function.

Since the rotation is quantised, it is quite possible that the molecule does not rotate at all if there is not enough energy.

It would be useful to know if a molecule like hydrogen or oxygen would rotate at room temperature.

The average rotation energy at a certain temperature is about $k_B T$. How does this compare with the energy levels?

The difference in energy between the $J = 0$ and $J = 1$ levels is

$$\Delta\varepsilon = \frac{\hbar^2}{I}$$

To have a reasonable fraction of the molecules in the first rotational state, this should be close to $k_B T$.

The rotational temperature

Equating $\Delta\varepsilon$ and $k_B T$, we find that T is given by

$$\theta_{\text{rot}} = \frac{\hbar^2}{Ik_B}$$

This called the "characteristic temperature of rotation," or the "rotational temperature." If the temperature is a lot lower than this, the molecules would hardly rotate.

The moment of inertia for diatomic molecules may be estimated using $I = mr^2$, where m is the mass of each atom and $2r$ the bond length. E.g.

For nitrogen, $\theta_{\text{rot}} = 2.8 \text{ K}$

For hydrogen, $\theta_{\text{rot}} = 82 \text{ K}$

So at room temperature, we would expect both to rotate.

It is interesting to note that if you put a bottle of hydrogen gas in liquid nitrogen (77 K), the molecules would hardly rotate at all!

For most gases at room temperature, the energy levels are very closely spaced compared to $k_B T$. The rotational partition function can be computed using an integral:

$$Z_{\text{rot}} = \int_{J=0}^{\infty} (2J + 1) \exp[-\hbar^2 J(J + 1)/2Ik_B T] dJ$$

The result is

$$Z_{\text{rot}} = \frac{T}{\theta_{\text{rot}}}$$

Note that this is a high temperature approximation, since we are assuming that $k_B T$ is much larger than the spacing between energy levels.

The rotational energy at high temperature is then given by

$$U = Nk_B T^2 \frac{\partial \ln Z}{\partial T} = Nk_B T$$

and the rotational heat capacity by $C_{\text{rot}} = Nk_B$.

From translation to rotation

Imagine starting at a very low temperature for a diatomic gas, well below θ_{rot} .

There would be little rotation, just translational motion.

The heat capacity is the same as for monatomic gas:

$$C = \frac{3}{2}Nk_B = \frac{3}{2}nR.$$

Increase the temperature gradually. When you come close to θ_{rot} , the some molecules start to rotate.

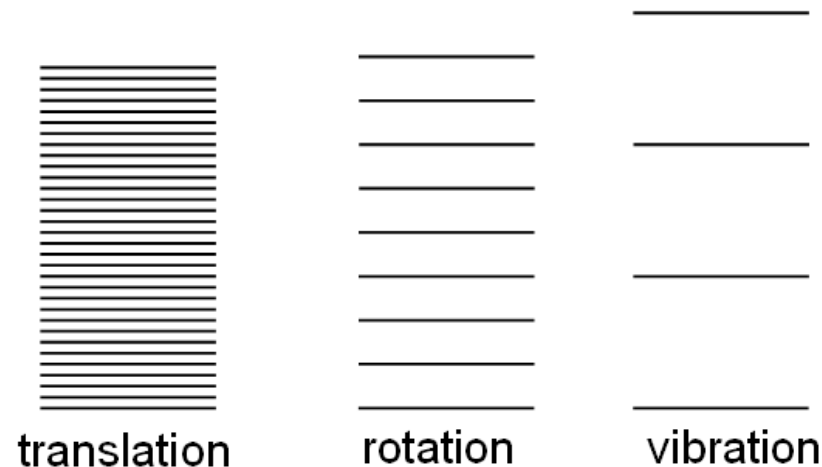
This would take up additional energy. So the heat capacity increases.

When the temperature gets much higher than θ_{rot} , the rotation would contribute an additional

$$C_{\text{rot}} = Nk_B = R.$$

From rotation to vibration

The spacing between energy levels for vibration tends to be much higher than those for rotation because of the strength of the bond.



Following a similar reasoning to rotation, there would be a "characteristic temperature of vibration," θ_{vib} . This is also called the Einstein temperature.

Below θ_{vib} , there would be little vibration.

If the temperature is much higher than θ_{vib} , the vibration would contribute to the heat capacity.

The atoms in a diatomic molecule can vibrate because of the bond between them. We may imagine that it acts like a spring. The behaviour is approximately the same as the 1-D simple harmonic oscillator that we have seen previously. The energy levels are:

$$E_n = \left(n + \frac{1}{2}\right) h\nu$$

where ν is the frequency.

The same formula for the partition function, energy and heat capacity may be used. The heat capacity is given by

$$C = Nk_B \left(\frac{\theta}{T}\right)^2 \frac{\exp(\theta/T)}{(\exp(\theta/T) - 1)^2}$$

where $\theta = h\nu/k_B$.

The heat capacity is given by

$$C = Nk_B \left(\frac{\theta}{T} \right)^2 \frac{\exp(\theta/T)}{(\exp(\theta/T) - 1)^2}$$

where $\theta = h\nu/k_B$.

θ is defined to be θ_{vib} , the "characteristic temperature of vibration":

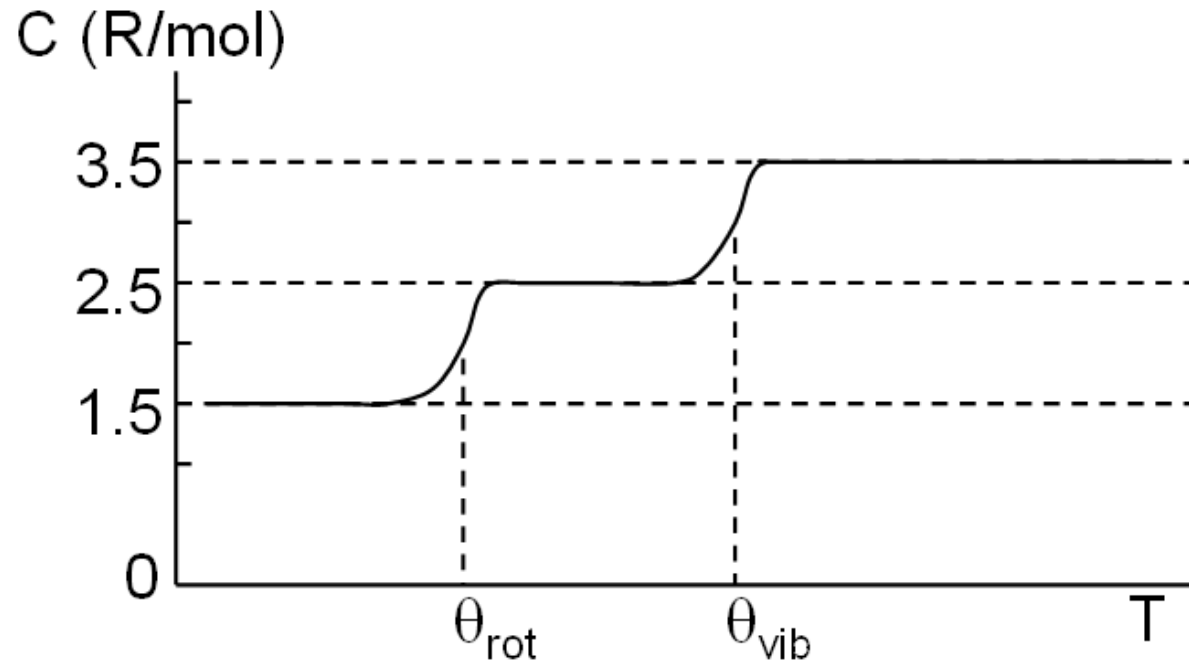
$$\theta_{\text{vib}} = h\nu/k_B.$$

If the temperature is much higher than θ_{vib} , the vibration would contribute to the heat capacity an additional

$$C \rightarrow C_{\text{vib}} = Nk_B.$$

Temperature dependance

Schematically, the heat capacity of a diatomic gas would vary with temperature in this way:

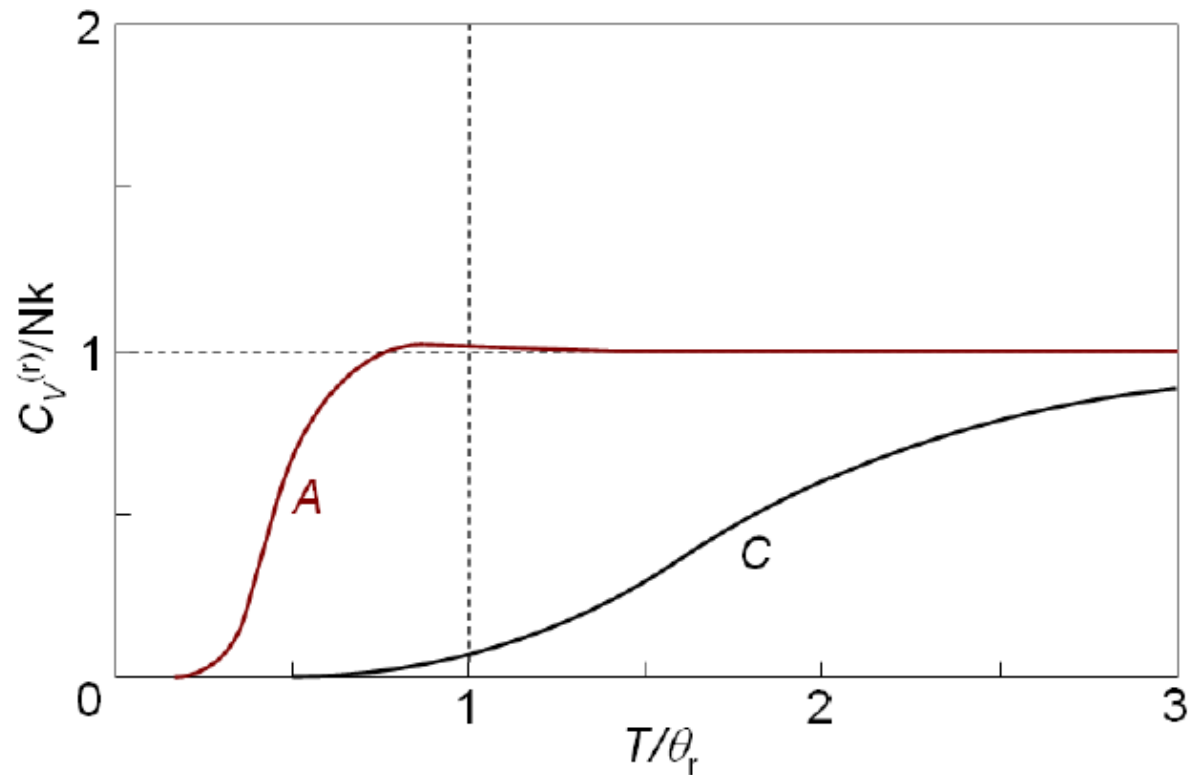


Experiments have shown that the heat capacities of real gases often follow this behaviour.

There are some exceptions, like hydrogen.

The heat capacity of hydrogen

According to the theory, the heat capacity of hydrogen should follow curve A.



Experiments show it follows curve C.

Spin states of hydrogen

The reason is because the protons in the nuclei of the molecule are fermions.

The spin states of the protons affects the rotational quantum number J . This in turn affects the rotational energy.

Protons are fermions. If the two protons are exchanged, the overall wavefunction must change sign.

The overall wavefunction is a product of the rotation wavefunction and the spin wavefunction (as well as electronic, vibration, ...).

When J is even, the rotation wavefunction remains the same when the protons are exchanged. So the spin wavefunction must change sign. This happens if the total spin is 0.

When J is odd, the rotation wavefunction changes sign when the protons are exchanged. So the spin wavefunction must remain unchanged. This happens if the total spin is 1.

The equilibrium case

The spin-0 molecule is called parahydrogen.

The spin-1 molecule is called orthohydrogen.

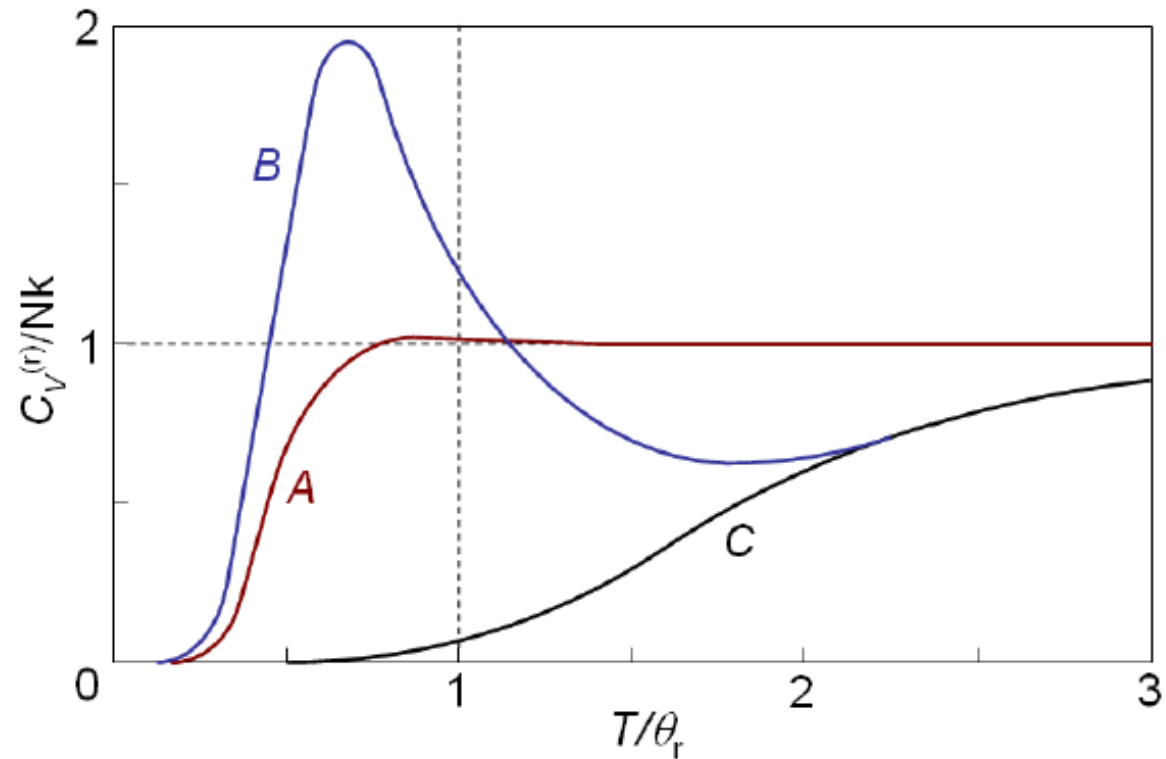
Assuming that the molecule can freely convert between the spin states, we can write down the partition function:

$$Z_{\text{rot}} = \sum_{J \text{ even}} (2J + 1) \exp(-J(J + 1)\theta_{\text{rot}}/T) \\ + 3 \sum_{J \text{ odd}} (2J + 1) \exp(-J(J + 1)\theta_{\text{rot}}/T)$$

where the factor of 3 comes from the degeneracy of the spin state 1.

If we now compute the heat capacity ...

... we get curve B.



The difference from C is even greater.

But they are not at equilibrium

The reason for the discrepancy is that in hydrogen gas, the probability for a molecule to change from ortho-hydrogen to para-hydrogen (or vice-versa) in a collision with another molecule is extremely low. Molecules tend to stay in their spin states.

If we take that into account, then we should treat the two components as different gases, each with their own rotational heat capacity

If ortho-hydrogen has three-times greater concentration in a sample than para-hydrogen (because of the degeneracy of the spin-1 state), then the total heat capacity will be:

$$C_{\text{rot}} = \frac{3}{4}C_{\text{ortho}} + \frac{1}{4}C_{\text{para}}$$

This heat capacity gives the curve C in the previous figure... in agreement with experiment, at last!

1. Density of states for particle in a box is

$$g(\varepsilon) = \frac{4m\pi V}{h^3} (2m\varepsilon)^{1/2}.$$

2. The Maxwell-Boltzmann distribution breaks down when at low temperatures.
3. "High temperature" means that $k_B T$ is much greater than the spacing between energy levels.
4. The heat capacity for one mole of monatomic gas is $3R/2$.
5. For diatomic gas, rotation contributes another R to the heat capacity at high temperature.
6. Vibration contributes a further R .
7. The partition function formula for entropy is different for distinguishable and indistinguishable particles.

4.7 Exercises

Exercise 1

Show that the partition function of an ideal gas:

$$Z = \int_0^\infty \frac{4m\pi V}{h^3} (2m\varepsilon)^{1/2} \exp(-\varepsilon/k_B T) d\varepsilon$$

is given by:

$$Z = V \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2}.$$

[You are given that

$$\int_{-\infty}^{\infty} x^{2n} e^{-a^2 x^2} dx = \frac{(2n)! \pi^{1/2}}{n! (2a)^{2n}}$$

]

First, move the constant factors outside the integral:

$$Z = \frac{4m\pi V}{h^3} (2m)^{1/2} \int_0^\infty \varepsilon^{1/2} \exp(-\varepsilon/k_B T) d\varepsilon$$

There is no power of 1/2 in the integration formula that is given. So we start with the substitution

$$\varepsilon = x^2$$

Then

$$\begin{aligned} Z &= \frac{4m\pi V}{h^3} (2m)^{1/2} \int_0^\infty x \exp(-x^2/k_B T) \cdot 2x dx \\ &= \frac{4m\pi V}{h^3} (2m)^{1/2} 2 \int_0^\infty x^2 \exp(-x^2/k_B T) dx \end{aligned}$$

Next, set n to 1 in the given formula:

$$\int_{-\infty}^\infty x^2 e^{-a^2 x^2} dx = \frac{2\pi^{1/2}}{(2a)^2 a}$$

The lower of limit of this integral is $-\infty$. To make this agree with the integral for the partition function Z ...

We change the lower limit to 0 and halve the right hand side, and the formula becomes:

$$\int_0^\infty x^2 e^{-a^2 x^2} dx = \frac{\pi^{1/2}}{(2a)^2 a}$$

Now comparing with the partition function again:

$$Z = \frac{4m\pi V}{h^3} (2m)^{1/2} 2 \int_0^\infty x^2 \exp(-x^2/k_B T) dx$$

the integrals become the same if we set

$$a^2 = \frac{1}{k_B T}.$$

Substituting this into the formula gives

$$\int_0^\infty x^2 e^{-x^2/k_B T} dx = \frac{\pi^{1/2}}{4} (k_B T)^{3/2}$$

Substituting this into partition function intergral, ...

We get

$$Z = \frac{4m\pi V}{h^3} (2m)^{1/2} 2^{\frac{\pi^{1/2}}{4}} (k_B T)^{3/2}$$

Simplifying,

$$Z = V \left(\frac{2m\pi k_B T}{h^2} \right)^{3/2}$$

we get the formula for the partition function.

Exercise 2

What is the root-mean-square speed of a helium atom at room temperature?

[Given that the relative atomic mass of helium is 4.
Atomic mass unit u is 1.6605×10^{-27} kg.
Boltzmann's constant k_B is 1.3807×10^{-23} J K⁻¹.]

First, we find the mean of v^2 . This can be obtained by

$$\bar{v^2} = \frac{1}{N} \int_0^\infty v^2 n(\varepsilon) d\varepsilon.$$

We have multiplied v^2 by the number particles at each energy interval $d\varepsilon$, and divided by the total number N .

The energy of the atom in an ideal gas is just the kinetic energy,

$$\varepsilon = \frac{1}{2}mv^2.$$

If we rewrite the above integral for v^2 in terms of the energy, we get

$$\bar{v^2} = \frac{2}{Nm} \int_0^\infty \varepsilon n(\varepsilon) d\varepsilon.$$

This integral is just the total energy U , i.e.

$$\bar{v^2} = \frac{2}{Nm} U.$$

We have previously obtained the energy U from the partition function:

$$U = \frac{3}{2}Nk_B T.$$

So the mean square speed is

$$\overline{v^2} = \frac{2}{Nm} \frac{3}{2} Nk_B T = \frac{3k_B T}{m}$$

The root-mean-square speed is then

$$\sqrt{\overline{v^2}} = \sqrt{\frac{3k_B T}{m}}.$$

We can now calculate the root-mean-square speed. The mass of the helium atom is

$$4u = 4 \times 1.6605 \times 10^{-27} = 6.642 \times 10^{-27} \text{ kg.}$$

Taking the room temperature as 298 K, the answer is

$$\begin{aligned}\sqrt{v^2} &= \sqrt{\frac{3k_B T}{m}} \\ &= \sqrt{\frac{3 \times 1.3807 \times 10^{-23} \times 298}{6.642 \times 10^{-27}}} \\ &= 1363 \text{ m/s}\end{aligned}$$

Exercise 3

Given that the internuclear separation in the O_2 molecule is 1.2 \AA , calculate its characteristic temperature of rotation.

[The relative atomic mass of the oxygen atom is 16.

Atomic mass unit u is $1.6605 \times 10^{-27} \text{ kg}$.

Planck's constant \hbar is $1.0546 \times 10^{-34} \text{ J s}$.

Boltzmann's constant k_B is $1.3807 \times 10^{-23} \text{ J K}^{-1}$.]

The characteristic temperature of rotation is given by

$$\theta_{\text{rot}} = \frac{\hbar^2}{Ik_B}.$$

I is the moment of inertia, given by

$$I = \sum mr^2.$$

r would be the distance from the centre of the molecule to each atom, i.e.

$$r = 1.2/2 = 0.6\text{\AA},$$

and the mass is

$$m = 16u = 16 \times 1.6605 \times 10^{-27} = 2.657 \times 10^{-26} \text{ kg}.$$

The O_2 molecule has 2 atoms. So the moment of inertia is

$$\begin{aligned} I &= 2mr^2 = 2 \times 2.657 \times 10^{-26} \times (0.6 \times 10^{-10})^2 \\ &= 1.913 \times 10^{-46} \text{ kg m}^2. \end{aligned}$$

The characteristic temperature of rotation is given by

$$\begin{aligned}\theta_{\text{rot}} &= \frac{\hbar^2}{Ik_B} \\ &= \frac{(1.0546 \times 10^{-34})^2}{1.913 \times 10^{-46} \times 1.3807 \times 10^{-23}} \\ &= 4.21 K.\end{aligned}$$

Exercise 4

The Einstein temperature (the characteristic temperature of vibration, θ_{vib}) of O_2 is 2200 K. Calculate the percentage contribution of the vibrations to its heat capacity at room temperature.

The energy levels of the 1-D simple harmonic oscillator are given by

$$E_n = (n + 1/2)h\nu.$$

where ν is the frequency of vibration. The Einstein temperature is defined by

$$\theta_{\text{vib}} = h\nu/k_B,$$

As room temperature is much lower than this, we may expect most of the molecules would be at the lowest level E_0 . Perhaps a very small number would be excited to the next level E_1 .

We can use this idea to estimate the vibrational heat capacity at room temperature.

So we would be interested into only 2 levels, E_0 and E_1 . The spacing in between is $h\nu$.

The probability of a particle at one level is proportional to the Boltzmann factor. Since most of the particles are at E_0 , the probability of finding a particle there is close to 1. So the probability of finding a particle at E_1 would be given by the Boltzmann factor $\exp(-h\nu/k_B T)$.

This means that the number of particles in:

E_1 is $n_1 = N \exp(-h\nu/k_B T)$, and
 E_0 is $n_0 = N - N \exp(-h\nu/k_B T)$.

Because $\exp(-h\nu/k_B T)$ would be very small, the total is still close to N . The total energy is then

$$\begin{aligned} U &= n_0 E_0 + n_1 E_1 \\ &= \frac{1}{2} h\nu (N - N \exp(-h\nu/k_B T)) + \frac{3}{2} h\nu N \exp(-h\nu/k_B T) \\ &= \frac{1}{2} h\nu N (1 + 2 \exp(-h\nu/k_B T)) \end{aligned}$$

The heat capacity is then

$$\begin{aligned} C &= \frac{dU}{dT} \\ &= h\nu N (h\nu/k_B T^2) \exp(-h\nu/k_B T) \\ &= N k_B (h\nu/k_B T)^2 \exp(-h\nu/k_B T) \end{aligned}$$

In terms of the Einstein temperature,

$$\theta_{\text{vib}} = h\nu/k_B,$$

the heat capacity is

$$C = Nk_B(\theta_{\text{vib}}/T)^2 \exp(-\theta_{\text{vib}}/T))$$

This would be valid at temperatures much lower than θ_{vib} , such as room temperature. At 298 K, the vibration heat capacity is then given by

$$C_{\text{vib}} = Nk_B(2200/298)^2 \exp(-2200/298) = 0.0339Nk_B$$

At room temperature, the heat capacity mainly consists of translational and rotational contributions, which gives

$$C = \frac{3}{2}Nk_B + Nk_B = \frac{5}{2}Nk_B$$

Therefore the percentage contribution of the vibrations to the heat capacity at room temperature is

$$0.0339 \div \frac{5}{2} = 13.6$$